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Partial molar entropy of electrons in a jellium model: Implications for thermodynamics of ions in solution and electrons in metals

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ABSTRACT

A universal relationship between the partial molar entropy of electrons in a conductor and the absolute thermoelectric power of the conductor was previously established using macroscopic thermodynamics. This relationship may depend on temperature but not on the type of material. Building on this, a recent comment published in this journal, as well as some earlier work, has argued that the partial molar entropy of electrons in a conductor is essentially equivalent to the absolute thermoelectric power of the metal. The argument was based on the thermodynamic and transport properties of a free electron Fermi gas. To further validate the relationship the present paper extends this approach to a jellium model of electronic structure. If the proposed equivalence between partial molar entropy and absolute thermoelectric power is valid it opens the way for an experimental thermodynamic method to measure quantities that have previously been considered un-measurable, such as partial molar entropies of ions in solution and electric fields in homogeneous conductors placed in a temperature gradient. It also relates to questions about the completeness of current thermodynamic theory and the possibility of a new principle or law of thermodynamics.

1. Introduction

An earlier paper in this journal discussed thermoelectrochemical effects and also examined the relationship between the partial molar entropy of electrons in metals and the absolute Seebeck coefficient of the metal, also known as the absolute thermoelectric power [1]. By applying microscopic theory to the problem it was argued that the partial molar electronic entropy and the absolute thermoelectric power are essentially equivalent for all isotropic materials.

Stated briefly, the argument for the validity this proposal uses Eq. (1)

$$G(T) = S + F\sigma \tag{1}$$

where S is the partial molar entropy of electrons in the metal, F is Faraday's constant, and σ is the absolute Seebeck coefficient of the metal. In this equation $G(T)$ is a universal function, i.e. the same for all materials. In the limit of infinite number density both S and σ become zero for a degenerate free electron Fermi gas. This implies that $G(T)$ is also zero. Since $G(T)$ is a universal function, if $G(T)$ must be zero for one isotropic material it is true for all isotropic materials, and one concludes that

$$S = -F\sigma \tag{2}$$

for all isotropic materials. In plain language this relationship means that the partial molar entropy of electrons in a metal is essentially equivalent to the absolute Seebeck coefficient of the metal.

Earlier work also concluded that the partial molar entropy of the electron and the absolute thermoelectric power are essentially equivalent [2,3]. The restriction to isotropic materials has been discussed by Tykodi [2].

As noted above, the relationship summarized in Eq. (2) was derived by considering the thermodynamic properties of a free electron Fermi gas. However, it is good practice to validate a scientific result using more than one line of evidence. Therefore, the present paper takes this analysis one step further to consider the jellium model of electronic structure, which is more similar to a real metal than the free electron model. The jellium model answers certain objections that could be raised against the free electron Fermi gas model.

2. Theoretical development

Because $G(T)$ is a universal function for all materials, the question of whether a particular method of evaluating $G(T)$ is valid or not depends, in part, on what one means by the term "material".

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If one is using a theoretical construct for the test material then an important question is whether the theoretical material has properties that are sufficiently similar to real materials to consider the material as a valid test case. For example, if the argument from Ref. [1] for Eq. (2) of the present paper were to fail, it would be because the physical model upon which it was built (a strongly degenerate free electron Fermi gas) had somehow failed to capture some essential feature of real materials.

The free electron Fermi gas differs from real conductors in several respects. (1) It does not include electron–phonon interactions. (2) It does not include interactions of electrons with a periodic lattice. (3) It does not include electron–electron interactions.

Although some investigators may consider that an analysis of the problem based on the free electron Fermi gas is sufficient to validate Eq. (2), (the present author included,) for other investigators the differences between the free electron gas model and real materials could open objections to using this model to validate Eq. (2). In particular one could ask "Is the degenerate free electron Fermi gas similar enough to real materials to be used to validate Eq. (2)?" Therefore, let us examine the three issues above, starting with electron–phonon interactions.

It is well known that acoustic properties and electronic structure vary between one material and another. Clearly, electron–phonon coupling must therefore vary between one material and another, and since $G(T)$ does not depend on the material, it must mean that $G(T)$ does not depend on electron–phonon interactions.

Next, let us consider the interactions of electrons with a periodic lattice. Lattice properties vary greatly from one conductor to another. Some conductors, such as liquid metals, do not even have a periodic lattice. Therefore, $G(T)$ cannot depend on lattice periodicity.

There is still the possibility that $G(T)$ could depend, in a general way, on the existence of a background of positive charge which interacts with the electrons, even if lattice periodicity is not a factor. Therefore, if one is to go beyond the free electron Fermi gas model to validate Eq. (2) one should use a model in which electrons interact with a background of positive charge. One should also include electron–electron interactions. The simplest system which includes these interactions is the uniform electron gas model, also known as the jellium model. In this model electrons interact with each other as well as a uniformly distributed positive charge.

The thermodynamics of this model can be analyzed in the light of a landmark paper by Kohn and Sham [4]. That paper builds upon earlier results from Hohenberg and Kohn [5] to derive a set of equations they describe as a Hartree–Fock method, corrected for correlation effects, and applies these results, together with a finite temperature generalization from Mermin [6] to analyze the thermodynamics of an interacting Fermi gas. In Section 3 of [4] the authors show that within the approximations employed in their paper the thermodynamics of an electron gas in a potential $v(r)$ can be treated in much the same way as a free particle system in an effective potential shifted relative to that of a free particle system of the same number density.

At high number density the energy per electron of a homogeneous electron gas in the ground state is given by:

$$E = \frac{A_F}{r_s^2} - \frac{B_E}{r_s} + C_C \ln(r_s) - D_C \tag{3}$$

where the term containing A_F is the energy of a degenerate free electron gas, the term containing B_E is the exchange energy, the terms containing C_C and D_C represent the correlation energy, and r_s is the Wigner–Seitz radius, which in the case of a jellium is the radius of a sphere whose volume is equal to the mean volume per electron. In atomic units, A_F and B_E have values of 2.21 and 0.916 respectively. The value of C_C is variously quoted as 0.0313 or 0.0622, depending on the source, and the value of D_C is variously quoted as 0.115 or 0.096, depending on the source [7–10].

If N is the total number of electrons then the total energy of the ground state is

$$E_{Total} = \frac{NA_F}{r_s^2} - \frac{NB_E}{r_s} + NC_C \ln(r_s) - ND_C \tag{4}$$

Considering the relationship between the Wigner–Seitz radius, particle number, and volume

$$\frac{4\pi}{3} r_s^3 = \frac{V}{N} \tag{5}$$

one can re-write the total energy as

$$E_{Total} = N^{5/3} A_F \left(\frac{3V}{4\pi}\right)^{-2/3} - N^{4/3} B_E \left(\frac{3V}{4\pi}\right)^{-1/3} + NC_C ln\left(\left(\frac{3V}{4\pi N}\right)^{1/3}\right) - ND_C \tag{6}$$

Assuming that V is constant, the Fermi level at 0 K is

$$\mu_{T=0} = \frac{\partial E_{total}}{\partial N} \tag{7}$$

$$\mu_{T=0} = \frac{5}{3} N^{2/3} A_F \left(\frac{3V}{4\pi}\right)^{-2/3} - \frac{4}{3} N^{1/3} B_E \left(\frac{3V}{4\pi}\right)^{-1/3} + C_c \ln\left(\left(\frac{3V}{4\pi N}\right)^{1/3}\right) - \left(\frac{C_C}{3} + D_C\right) \tag{8}$$

$$\mu_{T=0} = \frac{5A_F}{3r_s^2} - \frac{4B_E}{3r_s} + C_c \ln(r_s) - \left(\frac{C_C}{3} + D_C\right) \tag{9}$$

The functional form of this expression is similar to that of the energy per electron (Eq. (3)) but with different constants. For example, it uses $5A_F/3$ in place of A_F. The leading term in Eqs. (8) and (9) is the zero temperature Fermi level of the degenerate free electron Fermi gas. One can see by inspection that as r_s approaches zero the free particle term dominates, and the other terms become negligible by comparison.

Given the fact that the electron density in a jellium is uniform, it seems reasonable to assume that the exchange and correlation energies of low-lying excited states should not be greatly different from those of the ground state. If this were strictly true, then the energy level spacing would be the same as the free particle spacing at the same density. In this case the density of states (which is inversely proportional to the energy level spacing) will show the same limiting form as the density of states of the free electron Fermi gas, and the analysis in Ref. [1] applies, leading to the same conclusion as before, namely that Eq. (2) of the present paper is valid.

Taking a different approach for estimating the density of states near the zero-temperature Fermi level, assume that the energy of promoting an electron from the highest occupied orbital (the zero temperature Fermi level) to the lowest unoccupied level is the same as the difference in energy between an N electron jellium and an $N+1$ electron jellium. This naïve assumption probably not strictly valid, but let us see where it leads

$$\Delta E_{N,N+1} = E_{Total,N+1} - E_{Total,N} = \sim \frac{\partial \mu_{T=0}}{\partial N} \tag{10}$$

$$\frac{\partial \mu_{T=0}}{\partial N} = \frac{10A_F}{9r_s^2 N} - \frac{4B_E}{9r_s N} - \frac{C_C}{3N} \tag{11}$$

The density of states is given by the inverse of the energy level spacing

$$\text{Density of states} = D(E_F) = \left(\frac{\partial \mu_{T=0}}{\partial N}\right)^{-1} \tag{12}$$

$$D(E_F) = \frac{N}{\frac{10A_F}{9r_s^2} - \frac{4B_E}{9r_s} - \frac{C_C}{3}} \tag{13}$$

In the limit of infinite electron number density (i.e. in the limit of zero Seitz radius), the first term in the denominator swamps the other terms, and the density of states becomes that of the degenerate free electron Fermi gas. The analysis based on the degenerate free electron gas therefore applies [1]. Briefly, both the partial molar entropy and the absolute thermoelectric power are proportional to temperature, and the proportionality constants for both approach zero as the density approaches infinity. Substituting this result into Eq. (1) gives the result that $G(T)$ is zero, implying the validity of Eq. (2).

Next, assume that the preceding equation is of the correct functional form but that the constants associated with the exchange and correlation terms (the analogs of the constants B_E and C_C) are different. In this case the first term in the denominator of the density of states equation still dominates as the electron gas density approaches infinity, and the density of states approaches that of the degenerate free electron Fermi gas. The analysis of Ref. [1] still applies, implying the validity of Eq. (2).

Next assume that the second term in the denominator depends not on r_s^{-1}, but on r_s^{-E}, where E is an arbitrary number not necessarily equal to one. In that case, as long as the condition

$$E < 2 \tag{14}$$

holds, the first term in the denominator still dominates as r_s approaches zero, the density of states approaches that of the degenerate free electron Fermi gas, and the analysis of Ref. [1] still applies, implying the validity of Eq. (2). An analogous argument applies to the last term in the denominator.

From the above development one sees that the assumptions about the exchange and correlation energies are not stringent in order for the analysis from Ref. [1] to apply. Furthermore, it is not necessary to assume that the exponent on the Seitz radius in the first term in the denominator (the free particle-related term) has a value of two. As long as the exponent in Eq. (13) is greater than zero and also greater than the exponent in the exchange-related term (parameter E in Eq. (14)) then the density of states will approach zero in the limit of zero Seitz radius. Therefore, it is reasonable to conclude that Eq. (2) is valid, and the partial molar electronic entropy is essentially equivalent to the absolute Seebeck coefficient.

Consider yet another way of looking at the problem. One can calculate that under the assumptions leading to Eq. (13) the ratio of the heat capacity of the interacting electron gas to the heat capacity of the non-interacting electron gas is given by the ratio of the density of states under for two models:

$$\frac{C_{interacting}}{C_{non-interacting}} = \frac{D(E_F)_{interacting}}{D(E_F)_{non-interacting}} = \frac{\frac{10A_F}{9r_s^2}}{\frac{10A_F}{9r_s^2} - \frac{4B_E}{9r_s} - \frac{C_C}{3}} \tag{15}$$

$$\frac{D(E_F)_{interacting}}{D(E_F)_{non-interacting}} = \left(1 + \frac{2B_E}{5A_F}r_s - \frac{3C_C}{10A_F}r_s^2\right)^{-1} \tag{16}$$

This ratio has also been calculated to higher accuracy by Gell-Mann, who obtained an expression of slightly different functional form [11]

$$\frac{C_{interacting}}{C_{non-interacting}} = \frac{D(E_F)_{interacting}}{D(E_F)_{non-interacting}} = (1 + 0.083r_s(-\ln r_s - 0.203) + \cdots)^{-1} \tag{17}$$

According to Gell-Mann this is an exact relationship for the first few terms of a series expansion. Gell-Mann also compared his result to an earlier approximate result obtained by Pines [12]

$$\frac{C_{interacting}}{C_{non-interacting}} = \frac{D(E_F)_{interacting}}{D(E_F)_{non-interacting}} = (1 + 0.083r_s(-\ln r_s + 1.47) + \cdots)^{-1} \tag{18}$$

Regardless of whether one uses Eqs. (16)–(18), or some other closely related equation, the qualitative result is the same. As the number density of the interacting gas approaches infinity the density of states approaches that of the degenerate free electron Fermi gas. Since the density of states of the degenerate free electron gas approaches zero one concludes that the heat capacity and entropy of the interacting electron gas (the jellium) approaches zero in the limit of infinite number density.

The partial molar electronic heat capacity and the partial molar entropy can be calculated as follows. The total heat capacity is related to the density of states by the following relationship

$$C_{total} = \frac{\pi^2 k_B^2}{3} D(E_F) T \tag{19}$$

where k_B is Boltzmann's constant. The total entropy is given by

$$S_{total} = \int_{T=0}^{T} \frac{C_{total}}{T} dT = \frac{\pi^2 k_B^2}{3} D(E_F) T = C_{total} \tag{20}$$

The two expressions are the same because of the particular functional form of C_{total}.

Partial molar quantities are given by

$$\frac{\partial C_{total}}{\partial N} = \frac{\partial S_{total}}{\partial N} = \frac{\pi^2 k_B^2}{3} \frac{\partial D(E_F)}{\partial N} T \tag{21}$$

Here we have written the partial molar quantities in terms of particle number, though it would more conventionally be expressed on a molar basis. One can express the density of states, $D(E_F)$, in the following form:

$$D(E_F)_{interacting} = D(E_F)_{non-interacting}(1 + f(r_s))^{-1} = \frac{9r_s^2 N}{10A_F}(1 + f(r_s))^{-1} \tag{22}$$

where $f(r_s)$ is taken from Eqs. (16)–(18) or a related equation that expresses the density of states in terms of the density of states of a free electron Fermi gas multiplied by a correction factor. For example

$$f(r_s) = \frac{2B_E}{5A_F}r_s - \frac{3C_C}{10A_F}r_s^2 \tag{23}$$

or

$$f(r_s) = 0.083r_s(-\ln r_s - 0.203) + \cdots \tag{24}$$

or

$$f(r_s) = 0.083r_s(-\ln r_s + 1.47) + \cdots \tag{25}$$

etc.

By making the appropriate substitutions into the equations above and calculating the partial derivatives one can verify that,

for any reasonable model for the density of states, the partial molar entropy of the interacting gas (the jellium model) approaches zero as the density approaches infinity.

3. Discussion

Let us consider whether the assumptions and approximations in treatment of the electron gas given by Kohn and Sham [4] would affect the arguments presented in the present paper. First, recognize that the requirement to invalidate the argument presented here is quite stringent. It is only necessary that the theory give a correct qualitative description for the argument presented here to be valid. It is not required that the equations predict the correct numerical values under all conditions, but only that the theory predicts the correct limiting values at zero Seitz radius, i.e. at infinite electron density.

Addressing the question of the applicability of the approach of Kohn and Sham, their theory is based on two principle approximations. One was that the lattice potential interacting with the electron gas is slowly varying. Being based on density of positive charge that is uniform throughout the material, the jellium model automatically satisfies that requirement. It is, in fact, the reference system relative upon which Kohn and Sham based their approximations. The second approximation made by Kohn and Sham is that the electron density is high. This requirement is automatically satisfied in the present paper because it is based on the limiting case of infinite particle density. Therefore, one can justify an opinion that the general approach of Kohn and Sham provides a reasonable way analyze the present problem, recalling that Kohn and Sham proposed that the thermodynamics of a real system of interacting electrons can be treated as similar to a system of non-interacting electrons subjected to an altered potential. Nevertheless, the assumptions and approximations of Kohn and Sham, as well as those by Gell-Mann, Pines, etc. should be critically examined by the community to see if there are any assumptions that could invalidate the arguments presented in this paper.

Note particularly the fact that Kohn and coauthors introduced the approach to electronic structure calculations known today as density functional theory (DFT). One of the properties of DFT is that, although quite accurate for the calculation of the ground state, the DFT orbitals is of uncertain physical significance. The scientific community should discuss whether those uncertainties would affect the conclusions of the present paper.

However, at least partially mitigating this uncertainty is that in the present paper a number of different approaches were used to estimate the density of states. It is not necessary that any of them are numerically correct at any finite number density. It only requires that they give the same result at infinite number density. All approaches lead to the same result at infinite number density, i.e. the density of states approaches that of the degenerate free electron Fermi gas, which in turn approaches zero under those conditions. This reduces them all to the problem of the previously discussed case, the degenerate free electron Fermi gas [1]. It is also worth mentioning that part of the arguments above were based on the works of Gell-Mann and Pines, and those papers preceded the papers by Kohn and coworkers by almost a decade and are therefore not dependent on the work of Kohn and Sham.

As mentioned earlier, it is generally a good practice to validate a result using as many ways as possible. Therefore, it would be very useful to consider other physical models in addition to the free electron model and the jellium model. For example, one might consider the properties of BCS superconductors and ask what would happen in BCS superconductor theory if one were to add a small number of electrons to the conductor. Would the total entropy increase, decrease, or be unaffected? Since the absolute thermoelectric power of all known superconductors is essentially zero [13], if BCS theory predicts a value of zero for the partial molar entropy this result would be another theoretical validation of Eq. (2).

Theoretical models that include band structure would also be of interest. As discussed in Ref. [1] and references contained therein it is known that the absolute thermoelectric power of some materials is positive, and for other materials it is negative. This would imply that the partial molar electronic entropy can be either positive or negative. If the partial molar entropy calculated from theoretical band structure calculations would mimic this feature, i.e. being either positive or negative, it would be consistent with the idea that the partial molar electronic heat capacity is equivalent to the absolute thermoelectric power. One could, perhaps, go a step further and compare theoretical calculations of the partial molar heat capacity with theoretical calculations of the absolute thermoelectric power. One potential challenge to overcome would be to assure that the inevitable approximations one would need to make in order to perform the calculations would not invalidate the comparison.

The gold standard for validating that the absolute thermoelectric power is equivalent to the partial molar electronic heat capacity would be calorimetric measurements of the partial molar electronic heat capacity. Conceptually, one would measure the heat capacity of a sample both before and after a change in the number of electrons in the sample. The results would be compared to thermoelectric parameters for the same material. In principle this type of experiment is possible, but the effect is expected to be exceedingly small, and with our present level of technology the experimental difficulties probably make this experiment impractical.

If Eq. (2) is valid then it would have several implications. The first is that it would provide a missing piece of information that would allow one to determine the partial molar entropy of ions in solution using electrochemical Peltier measurements. This was implicit by a rearrangement of the equations in Ref. [14] and was more explicitly stated in Ref. [1]. Summarizing the key relationships and concepts from Ref. [1], consider a generic electrochemical process under reversible conditions

$$M_{metal} \rightarrow M^{+}_{solution} + e^{-}_{metal} \tag{26}$$

The entropy of this process is given by two relationships. One comes from electrochemical Peltier heat measurements. The entropy of the process also equals the difference between the sum of the partial molar entropies of the products minus the partial molar entropy of the metal, Setting the experimentally entropy obtained by electrochemical Peltier measurements equal to the entropy expressed in terms of partial molar entropies, one can then use the partial molar entropy of the metal (i.e. the molar entropy obtained by third law measurements) and the partial molar entropy of electrons in the metal (obtained from the absolute thermoelectric power using Eq. (2)) to determine the partial molar entropy of ions in solution. Without a way to determine the partial molar entropy of electrons in the metal the problem of determining the partial molar entropy of ions in solution using this method is unsolvable. Eq. (2) provides the necessary information, turning an unsolvable problem into a solvable one.

A second implication is that it would imply that current thermodynamic theory might be incomplete. Briefly, Eq. (2) is a relationship between macroscopic thermodynamic functions. However, it seems that Eq. (2) cannot be derived or deduced from the currently accepted laws of thermodynamics. If Eq. (2) is valid and cannot be derived from existing thermodynamic theory then current thermodynamic theory is incomplete. If so then Eq. (2) itself could be considered to be one statement of the new principle. Ref. [1] discussed this rather ambitious proposal more fully and invited the wider scientific community to discuss it as well. If the proposed relationship between partial molar electronic entropy and absolute

thermoelectric power can be validated by direct experimental measurements, as discussed earlier in this paper, the implications regarding current thermodynamic theory would not be altered.

A third implication is that it would provide greater unity between the theories of reversible and irreversible thermodynamics. It does this by equating certain quantities between the two theories.

A fourth implication is that it would provide a way to determine the electric field within a conductor placed in a temperature gradient.

This fourth implication requires some explanation. Domenicali has shown that there is a relationship between the temperature coefficient of the electrochemical potential and the electric field existing within a conductor placed in a temperature gradient [15]

$$\Delta\varnothing = \frac{1}{e}\left(\frac{\partial\mu}{\partial T} + S^*\right)\Delta T \tag{27}$$

where $\Delta\varnothing$ is the electrostatic potential difference between two points at different temperature within the conductor, e is the absolute value of the electron charge, μ is the chemical potential of the electron, and S^* is the "transported entropy" of the electron.

Domenicali expressed his quantities on a per-particle basis rather than a molar basis. However, the equation is identical if expressed on a molar basis, provided one substitutes Faraday's constant in place of e in Eq. (27), yielding:

$$\Delta\varnothing = \frac{1}{F}\left(\frac{\partial\mu}{\partial T} + S^*\right)\Delta T \tag{28}$$

For small temperature and position differences the relationship between position and temperature is given by

$$\Delta T = \frac{\partial T}{\partial x}\Delta x \tag{29}$$

Substituting this into Eq. (28) and rearranging yields

$$E = \frac{\Delta\varnothing}{\Delta x} = \frac{1}{F}\left(\frac{\partial\mu}{\partial T} + S^*\right)\frac{\partial T}{\partial x} \tag{30}$$

By definition transported entropy is related to the absolute thermoelectric power by

$$S^* = -F\sigma \tag{31}$$

Substituting this into Eq. (29) and rearranging yields

$$E = \frac{\Delta\varnothing}{\Delta x} = \frac{1}{F}\left(\frac{\partial\mu}{\partial T} - F\sigma\right)\frac{\partial T}{\partial x} \tag{32}$$

Domenicali uses μ in a way that can be considered to be equivalent to the partial molar Gibbs free energy of a material in an environment independent of extrinsic electrostatic potentials. Its temperature coefficient therefore gives the partial molar entropy according to the following relationship

$$\frac{\partial\mu}{\partial T} = -S \tag{33}$$

Substituting this into Eq. (32) and rearranging gives an equation for the electric field inside a homogeneous material in the presence of a temperature gradient

$$E = \frac{\Delta\varnothing}{\Delta x} = -\frac{1}{F}(S + F\sigma)\frac{\partial T}{\partial x} \tag{34}$$

All of the quantities on the right-hand side are either constants or are experimentally accessible via generally recognized methods, except for S. Eq. (34) is a general thermodynamic relationship, and if a method is found to measure S (the partial molar electronic entropy of the metal) it would enable one to determine the electric field inside a homogeneous conductor placed in a temperature gradient.

Eq. (1) is also a general thermodynamic relationship. Substituting Eq. (1) into Eq. (34) yields

$$E = \frac{\Delta\varnothing}{\Delta x} = -\frac{G(T)}{F}\frac{\partial T}{\partial x} \tag{35}$$

However, as discussed above an argument has been presented in favor of Eq. (2) which relates partial molar entropy to thermoelectric power. Eqs. (1) and (2) combine to yield

$$G(T) = 0 \tag{36}$$

Substituting this into Eq. (35) yields

$$E = 0 \tag{37}$$

At the present time this seems to be the only way to evaluate the electric field in a homogeneous conductor in the presence of a temperature gradient. However, this result depends on the validity of Eq. (2), which as discussed above, has been proposed as an additional thermodynamic principle.

What if Eq. (2) is wrong? In that case the electric field in a metal in the presence of a temperature gradient is given by Eq. (35) without the result that $G(T) = 0$. In any case, because $G(T)$ is a universal function [1–3], the internal electric field must be the same for all conductors in a temperature gradient.

4. Conclusions

The thermodynamics of a jellium model provide a second way to evaluate the general relationship between the partial molar entropy and absolute thermoelectric power of a metal. It is shown here that the density of states of a jellium model approaches the density of states of a degenerate free electron Fermi gas as the number density approaches infinity. The thermodynamics of the jellium model therefore approach those of a degenerate free electron Fermi gas as the number density approaches infinity. Therefore, since it had been previously shown that for a degenerate free electron Fermi gas the absolute thermoelectric power is essentially equivalent to the partial molar electronic entropy, the same result must be true for a jellium, and since the relationship between the two quantities is universal the same result must be true for all materials. This result, if valid, provides a way to solve certain problems that have traditionally been considered unsolvable, such as measuring the partial molar entropies of ions in solution. It also implies that current thermodynamic theory may be incomplete and that an additional thermodynamic law or principle may be needed. Eq. (2) itself could serve as this new principle. This principle also provides a way to solve another problem that has traditionally considered unsolvable, determining the electric field in a homogeneous metal placed in a thermal gradient.

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